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**UNITED STATES PATENT APPLICATION**

of

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for

**INTERCONNECT STRUCTURE WITH INTERLAYER DIELECTRIC**

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1 **1. Related Applications**

2 This is a divisional US Patent Application Serial No. 09/143,289, filed on August  
3 28, 1998, titled "PLASMA TREATMENT OF AN INTERCONNECT SURFACE DURING  
4 FORMATION OF AN INTERLAYER DIELECTRIC ", which is incorporated herein by  
5 reference.

6  
7 **BACKGROUND OF THE INVENTION**

8 **2. The Field of the Invention**

9 The present invention relates to semiconductor chip processing. More particularly,  
10 the present invention relates to formation of interlayer dielectrics that cover electrically  
11 conductive interconnects. In particular, the present invention relates to a method of resisting  
12 oxidation from the top surface of an electrically conductive interconnect during the formation  
13 of an interlayer dielectric.

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15 **3. The Relevant Technology**

16 In the microelectronics industry, a substrate refers to one or more semiconductor  
17 layers or structures which includes active or operable portions of semiconductor devices. In  
18 the context of this document, the term "semiconductive substrate" is defined to mean any  
19 construction comprising semiconductive material, including but not limited to bulk  
20 semiconductive material such as a semiconductive wafer, either alone or in assemblies  
21 comprising other materials thereon, and semiconductive material layers, either alone or in  
22 assemblies comprising other materials. The term substrate refers to any supporting structure  
23 including but not limited to the semiconductive substrates described above.

24 Semiconductor chip processing technology involves miniaturizing a plurality of  
25 semiconductive devices and placing them side-by-side upon a wafer. As miniaturization  
26 technology progresses, it has become expedient to stack semiconductive devices in order to

1 retain a small chip footprint. It is also necessary to connect stacked devices by way of  
2 formation of an interconnect corridor and by filling of the interconnect corridor with  
3 electrically conductive material such as a tungsten stud. Metallization lines are formed that  
4 make electrical connection to the tungsten stud. These metallization lines need to be  
5 electrically isolated from semiconductive devices that are formed above an existing layer of  
6 semiconductive devices. To this end, an interlayer dielectric (ILD) such as an oxide or  
7 nitride is formed.

8 Figure 1 is an elevational cross-section view of a semiconductor structure 10 that  
9 depicts interconnects 12 within a dielectric layer 14. Semiconductor structure 10 has an  
10 upper surface 16 upon which an interlayer dielectric (ILD) layer 18 has been formed. The  
11 left half of Figure 1 depicts an initial effect of formation of ILD layer 18 according to the  
12 prior art. It can be seen that the portion of interconnect 12 that was exposed as part of upper  
13 surface 16 of semiconductor structure 10 has formed an oxide husk 20 upon interconnect 12.  
14 Oxide husk 20 is formed either after planarization to form upper surface 16, such as by  
15 chemical-mechanical planarization (CMP) or during the deposition of ILD layer 18. Where  
16 interconnect 12 is a tungsten plug, oxide husk 20 forms into tungsten oxide ( $WO_3$ ).

17 Further processing of semiconductor structure 10, including thermal processing,  
18 causes complications that arise in the prior art. The right half of Figure 1 depicts one prior  
19 art problem. It can be seen that, due to a large stress between oxide husk 20 and interconnect  
20 12, oxide husk 20 has delaminated from interconnect 12 due to adhesion failure, and pushed  
21 upwardly to form a void 22 immediately above interconnect 12. Void 22 causes planarity  
22 problems and can also lead to underetched trenches prior to metal fill. The delamination of  
23 oxide husk 20 is an indication of a relatively thick oxide over interconnect 12. The thickness  
24 of oxide husk can range from about  $10\text{\AA}$  to about  $500\text{\AA}$ . Oxide husk 20 needs to be removed  
25 prior to deposition of a metal line. The presence of void 22 causes a prominence in the ILD  
26 topology. The prominence can lead to underetched trenches prior to metal fill, resulting in

1 the metal line not making sufficient electrical contact with interconnect 12. In addition, the  
2 prominence caused by the formation of void 22 can be formed during ILD deposition.  
3 Additionally, the prominence formed due to void 22 could cause some imaging problems  
4 because of a departure from substantial planarity of the upper surface of the ILD.

5 The delamination of oxide husk 20 from upper surface 16 immediately above  
6 interconnect 12 creates significant yield problems and device failure both during device  
7 testing and in the field.

8 What is needed in the art is a method of overcoming the prior art problems. What  
9 is also needed in the art is a method of forming an ILD layer without the formation of an  
10 oxide husk and the subsequent formation of a void between the top of the interconnect and  
11 the ILD layer. What is needed in the art is a method of preventing or reducing the oxidation  
12 of the upper surface of a metallic interconnect during the formation of an interlayer dielectric.  
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Preferably, the chemical composition will be a nitrogen-containing chemical compound such as ammonia,  $\text{NH}_3$ . Where the interconnect is a refractory metal, such as tungsten, the at least one monolayer forms a tungsten nitride-type composition or adsorbed complex. Following formation of the at least one monolayer upon the upper surface of the

1 interconnect, formation of the ILD layer may be carried out by such methods as a deposition  
2 by the decomposition of tetra ethyl ortho silicate (TEOS), or by chemical vapor deposition  
3 (CVD) of oxides, nitrides, carbides, and the like.

4 In order to form an ILD layer using lower processing temperatures, it is preferred  
5 that a CVD be carried out under plasma-enhanced (PE) conditions, *i.e.*, PECVD.

6 Formation of the ILD layer may be carried out in a manner that introduces materials  
7 to form the ILD layer simultaneously with the introduction of the ammonia plasma to create  
8 a passivation layer upon the upper surface of the interconnect.

9 Next, formation of the ILD layer with substantially like materials is carried out under  
10 conditions where the ILD layer substantially absorbs the passivation layer and the passivation  
11 layer is sufficiently thick to resist substantial formation of the oxide husk.

12 Alternative compositions to ammonia may be used during plasma treatment of the  
13 upper surface of the interconnect. For example, nitrogen-containing compositions that are  
14 preferred for the inventive method include ammonia, diatomic nitrogen, nitrogen-containing  
15 silane, and the like.

16 These and other features of the present invention will become more fully apparent  
17 from the following description and appended claims, or may be learned by the practice of the  
18 invention as set forth hereinafter.

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surface according to the inventing methods such that the passivation layer has substantially protected the electrically conductive stud such that oxidation has been substantially resisted.

Figure 5 is an elevational cross-section view of the semiconductor structure depicted in Figure 4 after further processing, wherein a second depression has been formed into the ILD layer according to damascene technology in order to allow a metallization trench to be formed, or an upper level contact to be electrically connected to the interconnect that is beneath the ILD layer.



## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made to the drawings wherein like structures will be provided with like reference designations. It is to be understood that the drawings are diagrammatic and schematic representations of the embodiment of the present invention and are not drawn to scale.

The present invention relates to the formation of an ILD layer while preventing or reducing oxidation of the upper surface of an interconnect or contact stud. Prevention or reduction of oxidation of the upper surface of an interconnect is achieved according to the present invention by passivating the exposed upper surface of the interconnect prior to formation of the ILD.

In reference to Figure 2, prevention or reduction of the likelihood of oxidation of upper surface 16 of interconnect 12 is accomplished during the formation of ILD layer 18. This is carried out by an *in situ* passivation of upper surface 16 of interconnect 12, immediately prior to or simultaneously with the formation of ILD layer 18, avoids the problems of the prior art.

A preferred embodiment of the present invention, illustrated beginning at Figure 2, comprises providing semiconductor structure 10 consisting of dielectric layer 14. Following the formation of dielectric layer 14, a depression 26 is formed in dielectric layer 14 so as to terminate at an electrically conductive structure therebeneath such as a substrate 24. Depression 26 is then filled with an interconnect 12 as seen in Figure 3, composed of an electrically conductive material such as a refractory metal. Interconnect 12 can be a tungsten stud or the like. After filling of depression 26 with an electrically conductive material, upper surface 16 of interconnect 12 and upper surface 16 of dielectric layer 14 is formed by a method such as CMP as illustrated in Figure 3.

Following the formation of upper surface 16, a chemical composition is reacted with at least one monolayer of upper surface 16 of interconnect 12 to form a chemical compound having a higher resistance to oxidation than interconnect 12.

The chemical compound is provided in an amount sufficient to substantially chemically cover upper surface 16 of interconnect 12 in order to chemically protect approximately the first 1-1,000 atomic lattice layers thereof. The chemical compound may be a nitride form of the metal of which interconnect 12 is composed. Where ammonia, a hydrated nitrogen compound or the like is used, a chemical structure such as  $M-N-H_x$ , where M represents the metal of which interconnect 12 is composed.

The chemical compound may be, by way of non-limiting example, the nitrogen-containing chemical compound such as ammonia that has been adsorbed onto upper surface 16 of interconnect 12 sufficiently to substantially chemically cover or "blind off" substantially any chemically reactive portion of upper surface 16 of interconnect 12 during formation of ILD layer 18. Use of preferred chemical compounds that are to be matched with specific materials comprising interconnect 12 can be selected by one of ordinary skill in the art using such data and equations as Langmuir's monolayer adsorption isotherm or those also taught by Brunauer, Emmett, or Teller. Of interest to selection of a particular chemical compound in connection with a preferred material for interconnect 12, will be any one of the five types of adsorption isotherms as classified by Brunauer<sup>1</sup>.

It is of interest in the present invention that the formation of a passivation layer 32, as seen in Figure 3, substantially protects upper surface 16 of interconnect 12 from oxidation to a degree wherein the formation of oxide husk 20 and void 22 are substantially eliminated. Passivation layer 32 may be achieved by formation of a chemical compound upon upper surface 16 of interconnect 12 by a chemical reaction with approximately the first 1-1,000

<sup>1</sup> O. Hougen *et al.*, *Chemical Process Principles 2nd Ed., Chapter 10: Adsorption*, John Wiley and Sons, Inc. (1954).

1 atomic lattice layers of interconnect 12 or it may be achieved by adsorption onto upper  
2 surface 16 of interconnect 12 according to any of the aforementioned types as taught by  
3 Brunauer.

4 Preferably, the chemical composition will be a nitrogen-containing chemical  
5 compound such as ammonia,  $\text{NH}_3$ . Where interconnect 12 is a tungsten stud, the at least one  
6 monolayer reacts to form a tungsten nitride-type composition or adsorbed complex upon the  
7 at least one monolayer. Following reaction with the at least one monolayer of upper  
8 surface 16 of interconnect 12, formation of ILD layer 18 may be carried out by various  
9 methods. One method is deposition by the decomposition of tetra ethyl ortho silicate  
10 (TEOS), or by CVD of oxides, nitrides, carbides, and the like.

11 In order to form ILD layer 18 using lower processing temperatures, it is preferred  
12 that a CVD be carried out under plasma-enhanced conditions, *i.e.*, PECVD. According to  
13 the inventive method, PECVD temperatures are used in a temperature range from about  
14  $100^\circ\text{C}$  to about  $600^\circ\text{C}$ . Preferably, the processing temperature will be in a range from about  
15  $150^\circ\text{C}$  to about  $500^\circ\text{C}$ , more preferably from about  $200^\circ\text{C}$  to about  $450^\circ\text{C}$ , and most  
16 preferably  $300^\circ\text{C}$  to about  $400^\circ\text{C}$ .

17 According to the present invention, a first example is set forth below. Following the  
18 formation of dielectric layer 14, as illustrated in Figure 2, depression 26 such as a contact  
19 corridor is formed therein, exposing semiconductor substrate 24 that may be, by way of non-  
20 limiting example, a metallization line. Following the exposure of semiconductor  
21 substrate 24, a titanium liner layer 28 or the like is formed within depression 26.  
22 Subsequently, a titanium nitride layer 30 or the like is formed upon titanium liner layer 28.  
23 Titanium nitride layer 30 may be formed by thermal nitridation of a portion of titanium liner  
24 layer 28, by deposition of titanium nitride thereupon, or by a combination thereof.

1 Interconnect 12 is next formed within depression 26. A preferred material for  
2 interconnect 12 is tungsten or the like. Tungsten or the like may be formed within  
3 depression 26 by CVD, PECVD, or by physical vapor deposition (PVD).

4 Upper surface 16 as seen in Figure 3, may be formed by such methods as CMP or  
5 an anisotropic etchback that has an etch recipe selectivity that is substantially the same for  
6 interconnect 12 as for dielectric layer 14. By "substantially the same", it is meant that  
7 selectivity favors leaving dielectric layer 14, and favors it over interconnect 12 in a range  
8 from about 1.5:1, preferably about 1.2:1, more preferably 1.1:1, and most preferably 1.05:1.

9 Passivation of upper surface 16 of interconnect 12 is next carried out by placing  
10 semiconductor structure 10 within a tool such as a PECVD chamber and introducing and  
11 striking an ammonia plasma or the like therein. Treatment temperatures, as set forth above,  
12 are imposed upon semiconductor structure 10. The plasma treats upper surface 16 for a time  
13 treatment in a range from about 1 to about 60 seconds, preferably from about 5 to about 45  
14 seconds, more preferably from about 20 to about 40 seconds, and most preferably for about  
15 30 seconds.

16 Formation of ILD layer 18, as illustrated in Figure 4, may be carried out in a manner  
17 that introduces materials to form ILD layer 18 simultaneously with the introduction of the  
18 ammonia plasma to create a passivation layer 32 upon upper surface 16 of interconnect 12.  
19 Alternatively, after the formation of passivation layer 32 has been substantially  
20 accomplished, the deposition tool may be substantially evacuated of the ammonia plasma,  
21 and dielectric precursor materials may then be introduced to the deposition tool to form ILD  
22 layer 18. Other materials may be used to form passivation layer 32 besides ammonia. For  
23 example, diatomic nitrogen or a nitrogen-containing silane may be used. The specific  
24 material that may be used will depend upon the particular application.

25 Next, formation of ILD layer 18 with substantially like materials is carried out under  
26 conditions where ILD layer 18 substantially absorbs passivation layer 32 and or passivation

1 layer 32 is sufficiently thick to resist substantial formation of oxide husk 20. In this  
2 embodiment, it is preferred by way of non-limiting example that both passivation layer 32  
3 be formed using  $\text{NH}_3$  and ILD layer 18 be formed in a deposition by decomposition of TEOS.  
4 Other materials, however, may be chosen.

5 Completion of this example is carried out by the formation of second depression 34  
6 in ILD layer 18. Accordingly, a masking layer is patterned upon upper surface 36 of ILD  
7 layer 18 and an anisotropic etch is carried out to form second depression 34. The etch recipe  
8 is selective to interconnect 12 as well as titanium liner layer 28, titanium nitride layer 32, and  
9 optionally to dielectric layer 14.

10 Where formation of passivation layer 32 is carried out at least in part by adsorption,  
11 and where ammonia is used by way of non-limiting example, an ammonia compound and its  
12 derivatives are substantially adsorbed upon upper surface 16 of interconnect 12. By  
13 "substantially adsorbed" it is meant that passivation layer 32 does not volatilize during the  
14 time required to form ILD layer 18. This means that volatilization is prevented to an extent  
15 that passivation layer 32 resists formation of oxide husk 20, or a portion thereof. Of primary  
16 interest in the present invention is the achievement of an embodiment whereby passivation  
17 layer 32 sufficiently protects upper surface 16 of interconnect 12 such that during the  
18 formation of ILD layer 18, ILD layer sufficiently adheres to upper surface 16 of interconnect  
19 12 without causing structural failure as that experienced in the prior art.

20 Additionally and preferably, any component of passivation layer 32 that volatilizes  
21 during formation of ILD layer 18 will be soluble in the materials that form ILD layer 18 such  
22 that no immiscible gas bubbles form from volatilized materials of passivation layer 32.

23 A second example of the inventive method is set forth below. Semiconductor  
24 structure 10 includes dielectric layer 14, made of borophosphosilicate glass (BPSG).  
25 Dielectric layer 14 rests upon substrate 24. In this example, substrate 24 can be an  
26 electrically conductive film that is typically used to wire semiconductive devices.

1           Following the formation of dielectric layer 14, depression 26 is formed by an  
2   anisotropic dry etch that stops on substrate 24. The anisotropic dry etch may include such  
3   techniques as ion beam milling or an etch recipe that mobilizes a portion of the masking  
4   layer such that the masking layer redeposits upon the sidewalls of depression 26 while it is  
5   being formed, thereby forming a substantially anisotropic etch.

6           Following the formation of depression 26, titanium liner layer 28 is deposited upon  
7   dielectric layer 14 and substrate 24 preferably by PECVD. Titanium liner layer 28 is then  
8   partially treated in a thermal nitride environment in order to grow titanium nitride layer 30  
9   thereupon. Although titanium nitride layer 30 is grown by thermal combination and  
10   conversion of a portion of the titanium in titanium liner layer 28 into titanium nitride layer  
11   30, titanium nitride layer 30 may alternatively be formed by deposition of titanium nitride  
12   by such techniques as PVD, PECVD, CVD, and the like.

13          Following the formation of titanium nitride layer 30, interconnect 12 is formed by  
14   deposition of tungsten into depression 26. The deposition of tungsten into depression 26 in  
15   order to form interconnect 12 may be facilitated by the presence of titanium nitride layer 30  
16   and titanium liner layer 28. Where the formation of interconnect 12 is formed by force-  
17   filling of tungsten into depression 26, the presence of titanium nitride layer 30 and titanium  
18   liner layer 28 facilitate slippage of the tungsten material along the region of what will  
19   become upper surface 16 and into depression 26 so as to fill depression 26.

20          Following the filling of depression 26 with tungsten or the like in order to form  
21   interconnect 12, all tungsten that is not within depression 26 is removed by a technique such  
22   as CMP. Because CMP itself may form oxide husk 20, upper surface 16, particularly that  
23   portion of upper surface 16 that comprises interconnect 12, may need to be cleaned by such  
24   techniques as an interconnect oxide etch that is selective to dielectric layer 14 and  
25   unoxidized portions of interconnect 12.  
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Following the cleaning of upper surface 16, semiconductor structure 10 is placed within a deposition tool and an ammonia plasma is struck therein. Alternatively, the cleaning of upper surface 16 may be carried out within the same deposition tool where the ammonia plasma is struck. Additionally, the cleaning of upper surface 16 may be carried out within a cluster tool previous to *in situ* transfer of semiconductor structure 10 into the deposition tool. The temperature of semiconductor structure 10 during this stage of the inventive method is in a range substantially the same as in the previous example. Preferably, the treatment time to form passivation layer 32 is less than about 30 seconds. According to this second example, a preferred composition of passivation layer 32 comprises nitrogen that has been adsorbed upon upper surface 16 of interconnect 12 according to Brunauer's Type V adsorption. As a preferred alternative embodiment, upper surface 16 of interconnect 12 is first treated in a nitrogen atmosphere at a temperature sufficient to create tungsten nitride and then under conditions sufficient to create Type V adsorption of several layers of nitrogen compounds upon the tungsten nitride. By several layers of nitrogen compounds, it is understood that the overall composite thickness of passivation layer 32 is about 50Å, preferably about 20Å, more preferably about 10Å, and most preferably about 5Å.

Another example is set forth below. Processing is carried out as set forth in previous examples. The formation of passivation layer 32 is carried out *in situ* with the formation of ILD layer 18. After an optional cleaning of upper surface 16, semiconductor structure 10, within a deposition tool, is fed with a mixture of ammonia and silane or the like. At the beginning of this step of the inventive process, the mixture comprises an ammonia rich feed such that initially passivation layer 32 begins to form upon upper surface 16.

The removal of ammonia from the mixture may be carried incrementally. For example, the elimination of ammonia from the mixture may be initiated by decreasing the ammonia portion of the mixture by a preferred percentage of the entire amount of ammonia over a period of time. Specifically, the amount of ammonia may be decreased every five

1 seconds by about 5%, such that after about 100 seconds, the amount of ammonia in the feed  
2 mixture is reduced to about zero. Alternatively the amount of ammonia may be decreased  
3 every five seconds by 10%, such that after about one minute, the amount of ammonia in the  
4 feed mixture is reduced to about zero. Alternatively, the amount of ammonia may be  
5 decreased by about 25% every five seconds such that after about twenty seconds, the amount  
6 of ammonia in the feed mixture has been reduced to about zero. Additionally, the amount  
7 of ammonia may be decreased by 50% every five seconds such that after about ten seconds,  
8 the amount of ammonia in the feed mixture is reduced to about zero. Finally, the amount of  
9 ammonia in the feed mixture may be reduced to about zero after any five-second time  
10 increment to about zero from 100% ~~in a single step.~~

11 As an alternative embodiment and in connection with the reduction of the amount  
12 of ammonia in the mixture, processing conditions may be altered from conditions that are  
13 less likely to cause formation of oxide husk 20 to conditions that are more likely. For  
14 example, processing temperatures sufficient to form passivation layer 32 may be initiated  
15 with an ammonia-rich mixture under conditions not likely to cause formation of oxide husk  
16 20. As the amount of ammonia in the mixture is reduced, processing temperatures may be  
17 increased proportionally under conditions that are more likely to cause formation of oxide  
18 husk 20 than under conditions previously established when the amount of ammonia in the  
19 mixture is greater. The initial formation of some of passivation layer 32, however, resists  
20 the formation of oxide husk 20. Preferably, the processing temperature will be the same as  
21 the deposition temperature for ILD layer 18.

22 Following the formation of passivation layer 32, upper surface 16 is covered with  
23 ILD layer 18 *in situ* by a method as set forth above. During the deposition of ILD layer 18,  
24 passivation layer 32 protects upper surface 16 of interconnect 12 and prevents the formation  
25 of oxide husk 20. As a preferred alternative embodiment of the present invention, the  
26 materials comprising passivation layer 32 may react with ILD layer 18 material without



1 causing unwanted oxidation of upper surface 16 of interconnect 12. In this preferred  
2 alternative embodiment, the materials comprising passivation layer 32 and ILD layer 18 will  
3 interact to form a new compound that will have a lower stress than that of oxide husk 20.

4 Alternative compositions to ammonia may be used during plasma treatment of upper  
5 surface 16 of interconnect 12. For example, nitrogen-containing compositions that are  
6 preferred for the inventive method include ammonia, diatomic nitrogen, nitrogen-containing  
7 silane, and the like.

8 Figure 4 illustrates further processing of semiconductor structure 10 as depicted in  
9 Figure 3. It can be seen that ILD layer 18 has been formed upon upper surface 16 of  
10 semiconductor 10 according to the inventive method. The presence of passivation layer 32  
11 has prevented formation on oxide husk according to an object of the invention. It can be  
12 appreciated that passivation layer 32 may form exclusively upon interconnect 12 and  
13 alternatively onto titanium liner layer 28 and titanium nitride layer 30. This means that  
14 passivation layer 32 may not substantially form upon upper surface 16 over dielectric layer  
15 14 due to incompatible reaction chemistry that prevents any type of reactive material to form.

16 Following the formation of ILD layer 18, further processing is carried out as  
17 illustrated in Figure 5. Second depression 34 is formed into ILD layer 18 by patterning and  
18 etching thereof. In a damascene process such as that illustrated in Figure 5, second  
19 depression 34 is formed substantially above interconnect 12. Second depression may be, by  
20 way of non-limiting example, a wiring trench such that metallization within second  
21 depression 34 would run in and out of the plane of Figure 5. Additionally, second depression  
22 34 may be a contact corridor such that metallization would run left to right, substantially  
23 within the plane of Figure 5 along the upper surface 36 of ILD layer 18 and filled into second  
24 depression such that a metallization line with a contact is formed, whereby the contact is in  
25 electrical communication with interconnect 12.

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